



Nano particle LiFePO_4 prepared by solvothermal process



Li Wang^a, Wenting Sun^a, Xianyi Tang^b, Xiankun Huang^a, Xiangming He^{a,c,*}, Jianjun Li^a, Qingwu Zhang^b, Jian Gao^a, Guangyu Tian^c, Shoushan Fan^d

^a Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

^b China University of Mining & Technology, Beijing 100083, PR China

^c State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China

^d Department of Physics, Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, PR China

H I G H L I G H T S

- A glycol based solvothermal process is attempted to prepare nano LiFePO_4 cathode materials.
- The sample delivers capacity retention of 100% after 100 cycles at 100% depth of discharge.
- The sample presents an initial columbic efficiency of 98.9% and 100% during cycling afterward.
- The capacity of about 163 mAh g^{-1} at 0.1 C-rate, 157.8 mAh g^{-1} at 1 C-rate, and 145.9 mAh g^{-1} at 5 C-rate.

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A glycol based solvothermal process combined with carbon coating is attempted to prepare nano particle LiFePO_4 cathode materials for Li-ion batteries. Different concentration of starting materials, process time, pH values and process temperature are tried. Samples are characterized by XRD and SEM analysis. A carbon coating process with sucrose is used to make LiFePO_4/C composites. The optimized sample delivers capacity retention of 100% after 100 cycles at 100% depth of discharge with initial columbic efficiency of 98.9%, cycling capacity of about 163 mAh g^{-1} at 0.1 C-rate, 159 mAh g^{-1} at 0.5 C-rate, 157.8 mAh g^{-1} at 1 C-rate, and 145.9 mAh g^{-1} at 5 C-rate, under the electrode formula of 80% LiFePO_4/C composites, 10% carbon black and 10% binder. This study shows that proposed process can be a potential promising way to prepare high performance LiFePO_4 cathode materials for lithium ion batteries.

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1. Introduction

Lithium-ion batteries power many portable devices and in the future are likely to play a significant role in sustainable-energy systems for transportation and the electrical grid. According to the developing demands for Lithium-ion batteries, a good cathode material has to meet the following criteria: high capacity that can be retained for up to 1000 cycles; stability that can withstand fast recharge and discharge and other possible extreme conditions; affordability for consumer electronics and large scale storage, and

low toxicity. Olivine LiFePO_4 appears to meet many of these requirements when both its particle structure and surface chemistry are well tuned [1–5].

Though LiFePO_4 suffers low electronic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) and slow lithium ion diffusion coefficient ($\sim 1.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$), combination of carbon coating and size reduction have been proved to be an effective resolution [6,7]. LiFePO_4 nanoparticles are beneficial to enhance electrochemical reaction [8–11]. Besides particle size, the crystal orientation and crystal plane, so resulting in particle morphology, are also sensitive factors for LiFePO_4 of good performances [5,12,13].

The commercial success of new cathode materials mainly depends on the preparation method. It is more for LiFePO_4 material, according to the high requirements on morphology and structure control for high performances. Many preparation strategy, including solid state methods [14], sol–gel routes [15,16], and hydrothermal/

* Corresponding author. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 89796073; fax: +86 10 89796031.

E-mail addresses: hexm@tsinghua.edu.cn, hexiangming@tsinghua.org.cn (X. He).

solvothermal synthesis [11,17–19], have been employed to develop nanocomposite C/LiFePO₄ particles with controlled morphologies. However preparations involving solid-state reaction are energy intensive, poor in morphology control and batch stability. Fortunately, solution chemistry approaches, especially hydrothermal/solvothermal, are readily for crystalline structure tuning, high uniformity in products and processing, as well as employing relatively low temperature, and is considered to be a commercially viable approach [20].

However, assessing of solvothermal for industry is required. It is known that the formation of LiFePO₄ during hydrothermal/solvothermal experiences a heterogenous nucleation, namely dissolving-crystallization process [21–24], while nucleation, crystal growth and crystallization greatly depend on solvent, concentration, temperature, time, pH value et al. [25,26] Nevertheless, oversensitive reactions may lead to too high process cost on controlling. In this sense, solvent is very important due to its multiple roles during solvothermal. In particular, ethylene glycol is preferable for solvothermal synthesis of LiFePO₄. Firstly, the high viscosity may slow down the ion diffusion rate, and thus prevent the particles from growing. Secondly, as (010) plane is reported to be the most readily access surface for Li⁺ intercalation and is prominent in both calculated equilibrium and growth morphology, [27] ethylene glycol is helpful for (010) exposure due to its capping behavior on (010) plane and the low ion diffusion rate. In addition, ethylene glycol also plays an important role as a weak reducing agent to prevent the oxidation of Fe²⁺ to Fe³⁺, and this can ensure the purity of the product [28]. Though its price is not very low, considering of the recycling strategy, ethylene glycol based solvothermal is still promising for industry.

In this study, solvothermal is chosen as the synthetic method because of the feasibility of controlling the morphology and the accessibility of cheap raw materials, as well as relatively economic processing. To confirm the robustness of solvothermal process, effects of temperature, time, pH value, raw material ratio and concentration on LiFePO₄ nano-particles are assessed carefully. Our results show that uniform LiFePO₄ nanoparticles can be obtained in a wide temperature and time range. After a facile carbon-coating process, LiFePO₄/C composites conduct over 160 mAh g⁻¹ at 0.1 C rate.

2. Experimental

The precursor for LiFePO₄ is prepared by dissolving stoichiometric amounts of LiOH·H₂O, FeSO₄·6H₂O and H₃PO₄ (molar ratio 3:1:1) in glycol to form a solution (70 mL, corresponding to 0.2 mol L⁻¹ LiFePO₄), and then transferring the solution into a 100 mL Teflon-lined stainless steel autoclave for solvothermal treatment. To assess the influences of solvothermal conditions on the morphology and size of the LiFePO₄ particles, the solvothermal treatment are carried out at different temperatures or with different reaction times respectively. When the solvothermal reactions finish, the autoclave is cooled down naturally to room temperature and the reaction solution is washed by distilled water and dried at 80 °C.

To synthesize carbon-coated LiFePO₄ powders, LiFePO₄, sucrose (C₁₂H₂₂O₁₁) and deionized water (H₂O) are mixed in a weight ratio of LiFePO₄:C₁₂H₂₂O₁₁:H₂O = 20:1:2 and milled for 4 h in a mortar. The mixed slurry is dried and then sintered at 600 °C for 1 h in N₂. The carbon-coated LiFePO₄ powders are finally obtained. The residual carbon content determined by thermogravimetry is about 2 wt.%.

Powder X-ray diffraction (XRD, D/max-rB) using Cu Kα radiation is used to identify the crystalline phase. The sample morphology is observed by field emission scanning electron microscopy (SEM, JSM6301F).

Experimental test cells for measurements use the cathode with the composition of 80 wt.% LiFePO₄/C, 10 wt.% carbon black, and 10 wt.% PTFE. The separator is a Celguard 2400 microporous polypropylene membrane. The electrolyte is 1 M LiPF₆ EC + DEC (1:1 by volume). A lithium metal anode is used in this study. The cells are assembled in a glove box filled with argon gas. The charge–discharge cycling is galvanostatically performed at a current of 0.1–5.0 C with cut-off voltages of 2.75–4.2 V (versus Li/Li⁺) at room temperature. Discharge rate capability after charging at C/10 at upper cut-off voltage of 4.2 V. C/n denotes the rate at which a full discharge takes *n* hours. The loading density of the electrode is 17 mg cm⁻². The voltage window is 2.5–4.2 V.

3. Results and discussion

Processing temperature, duration, pH values, ratio of starting materials and concentration all greatly affect the dissolving-

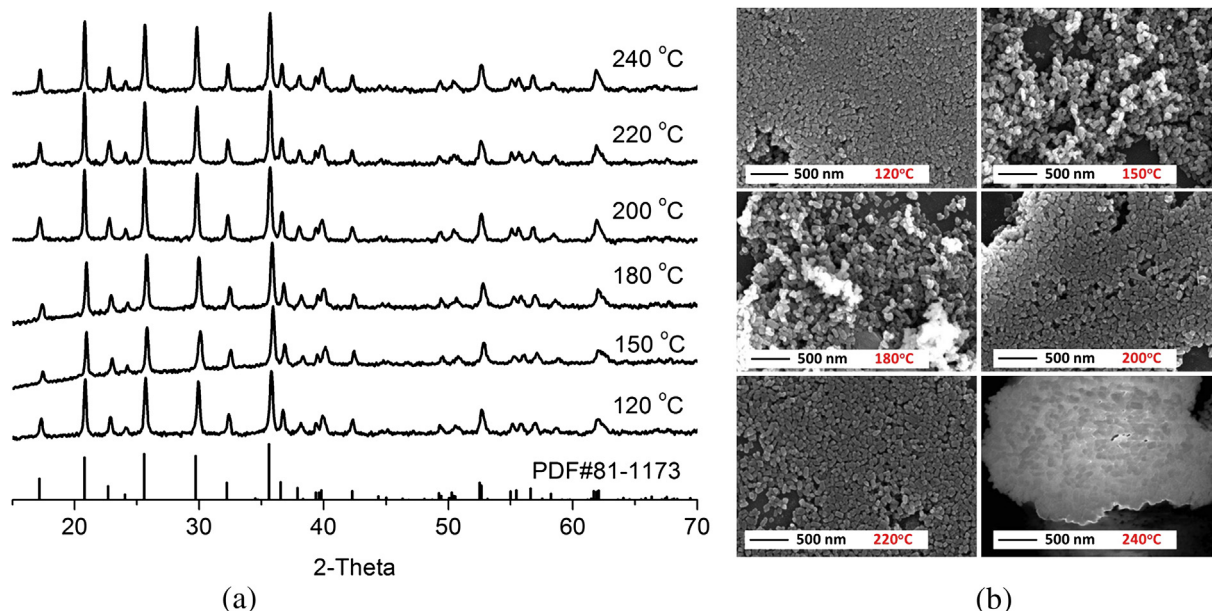


Fig. 1. The LiFePO₄ particles after glycol solvothermal reaction of 10 h at temperature of 120–240 °C (a) XRD patterns; (b) SEM images.

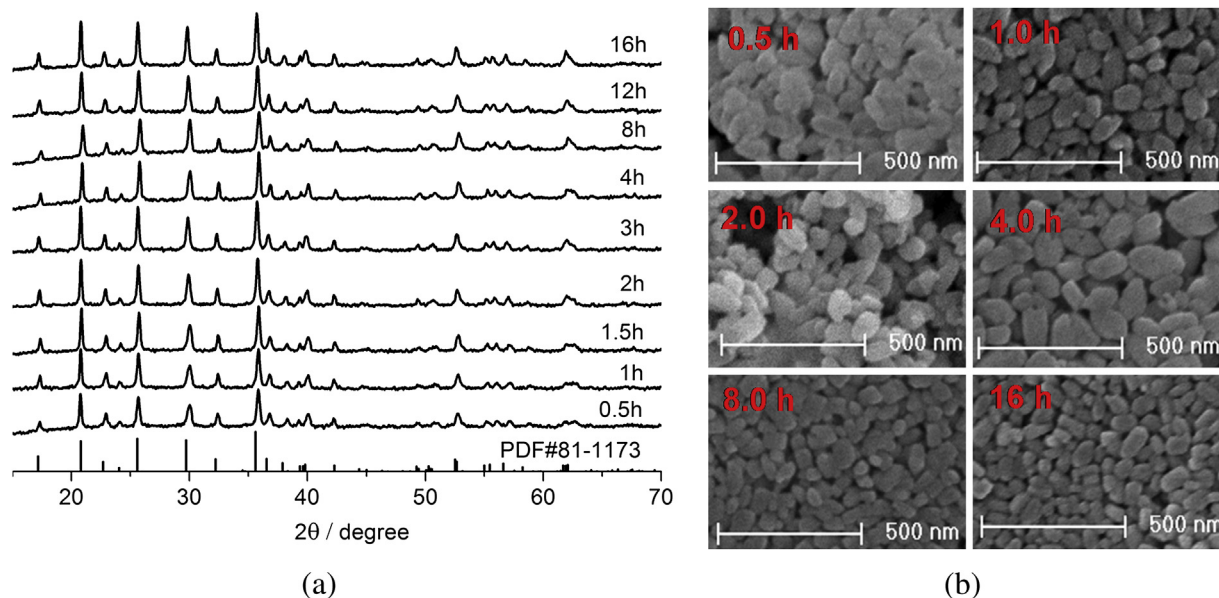


Fig. 2. The LiFePO_4 particles after glycol solvothermal reaction of different time at temperature of 180°C (a) XRD patterns; (b) SEM images.

crystallization during solvothermal process, resulting in variety of products [20,21,26]. However, the tolerance of products to temperature and time determines the reactor design and operation control. Usually, increasing temperature can enhance the precipitation and grain growth of the solid crystal in a solvothermal process, but can also bring weak point, such as energy consumption and safety issue, from the viewpoint of industrial production. 180°C is the most widely adopted temperature for hydrothermal/solvothermal synthesis of LiFePO_4 particles on the basis of many reports [11,17], so temperatures ranging from 120°C to 240°C is chosen to evaluate the variation of crystal structure and morphology of LiFePO_4 particles with temperature. Fig. 1(a) and (b) shows the XRD patterns and SEM images of the LiFePO_4 particles obtained at various reaction temperatures at a fixed reaction time of 10 h, respectively. It can be observed that crystalline LiFePO_4 forms even at 120°C , indicating ethylene glycol can act as reductant even when temperature is only 120°C . Besides, all the XRD patterns are consistent with JCPDS (81-1173) standard olivine LiFePO_4 patterns. This observation confirms that LiFePO_4 samples can be

prepared with high purity and considerably good crystallization in the whole temperature range, using ethylene glycol as reaction medium at different temperatures. Based on above analysis, the strong steady of olivine structure with temperature can be deduced, implying that an easy control on temperature field may be acceptable for the design of chemical caldron. All the LiFePO_4 particles are tiny cuboids, and their morphologies keep almost constant with temperature increasing, as shown in Fig. 1b. Except that particles prepared at 240°C aggregate, the other samples prepared at lower temperatures are all well mono-dispersed. LiFePO_4 samples prepared at different temperature present similar size of about 60–100 nm long and 30–50 nm wide, indicative a little effect of temperature. This result again supports the steady of olivine LiFePO_4 formation and crystallization to temperature. These results are quite different with related observations on hydrothermal, where both particle size and morphology generally present dramatic changes with temperature varying [21,23]. The strong dependency of LiFePO_4 nucleation and crystal growth on process temperature endow hydrothermal with flexibility to produce

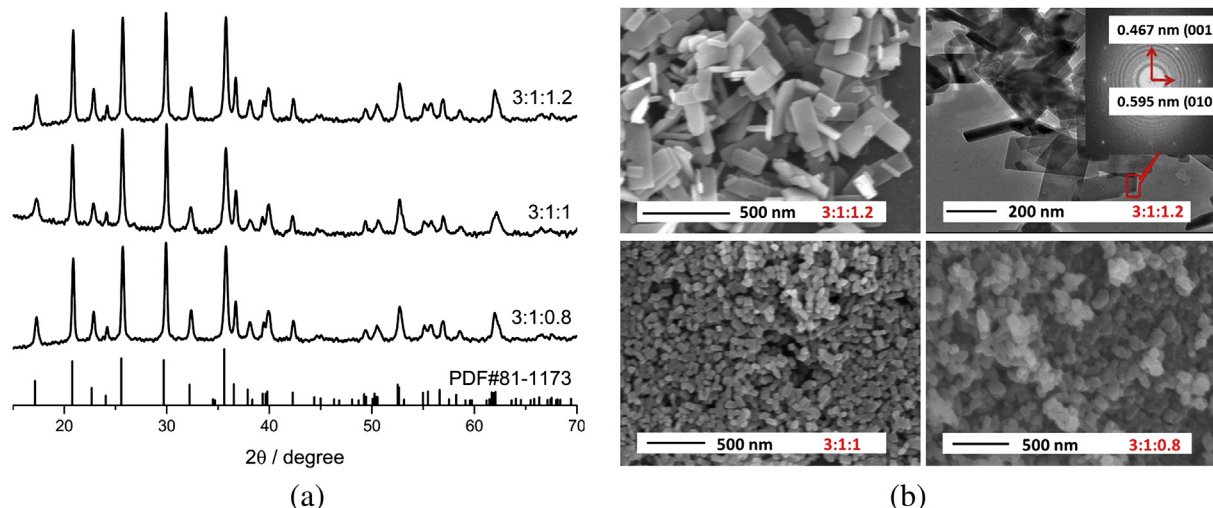


Fig. 3. LiFePO_4 particles prepared with different mole ratio of reactants, with $[\text{Fe}^{2+}] = 0.2\text{ M}$ at 180°C for 10 h (a) XRD patterns; (b) SEM and TEM images.

Table 1
Atomic ratio of reactants and as-prepared LiFePO₄.

Samples	A	B	C
	Li:Fe:P (mole)	Li:Fe:P (mole)	Li:Fe:P (mole)
Reactants	3:1:0.8	3:1:1	3:1:1.2
As-prepared LiFePO ₄	1.155:1:0.953	1.113:1:0.999	1.026:1:0.781

various LiFePO₄ particles, while it in turn brings high difficulty for process control.

As mentioned before, 180 °C is the widely adopted temperature for LiFePO₄ preparation. Then the effect of process time on crystallization and morphology of LiFePO₄ is investigated with a fixed synthesis temperature of 180 °C, as shown in Fig. 2. Crystalline LiFePO₄ can form within 0.5 h without any impurities, which can be detected by XRD analysis. It can be observed that the crystallinity of LiFePO₄ particles enhances obviously after 1.5 h and keeps almost constant in longer time, according to the XRD patterns (Fig. 2a). Then very strict control on time may be not quite necessary during processing in view of crystallinity. However, cases for morphology and particles size are different. With process time increasing, the morphology changes gradually, and the average particle size varies obviously. For example, LiFePO₄ particles prepared within 1 h present average particle size of 100 nm long and 50 nm wide, while become around 150 nm long and 80 nm wide when the process time is increased to 4 h, similar morphology, and become about 80 nm long and 30 nm wide when the process time is longer than 8 h. Fortunately, LiFePO₄ particles prepared with different times are all highly dispersive and shows a very narrow size distribution. Though process time dose show a slight effect on morphology and grain size of LiFePO₄ particles, the constancy of olivine LiFePO₄ formation and crystallization to process time is still quite acceptable in view of application. For hydrothermal, morphology and grain size of LiFePO₄ particles also show less dependency on process time when compared with that on temperature. However, the changes in average particles size and size distribution are so dramatic that a careful process control is considerably necessary for high quality products and high batch uniformity. The differences between solvothermal and hydrothermal may come from the

difference in ion diffusion rate, that is low ion diffusion rate results in low crystal growth [28].

Though the requirements on temperature control and time control of a reaction are of the most importance for design of a tank reactor, the ratio of raw material, concentration and pH value are also key factors determine the species, crystal phase, morphology and yield. As reported, the mole ratio of Li:Fe:P associates with electrochemical performances can be considered as a criterion for purity evaluation of LiFePO₄ product. Then the dependency of LiFePO₄ purity on mole ratio of the reactants is investigated, as shown in Fig. 3 and Table 1. Here, only the portion of H₃PO₄ is considered because it is reported to be associated strongly with particle size [18], yield [25] and Fe³⁺ impurities [21] in hydrothermal. When the Li:Fe:P changes from 3:1:0.8 to 3:1:1.2, the XRD patterns of the as-prepared LiFePO₄ particles are similar in both peak position (Fig. 3a), indicative of the pure olivine LiFePO₄ according to JCPDS (81-1173). However, the corresponding SEM micrographs disclose significant changes in particle morphology and size distribution. As can be observed from Fig. 3b, LiFePO₄ prepared with Li:Fe:P = 3:1:1.2 is rectangle in shape, 20–30 nm thick, 200–300 nm long and 100–150 nm wide. The TEM image confirms the high tidiness and high dispersity of these nano-flakes, and the most exposed surface seems to be (100) plane as determined by electron diffraction patterns. However, LiFePO₄ prepared with Li:Fe:P = 3:1:1 and Li:Fe:P = 3:1:0.8 remain the short rod-like morphology, though the particles size of the latter is about twice larger than the former. The corresponding Li:Fe:P in the final LiFePO₄ product also varies greatly with different reactant ratio, as shown in Table 1. LiFePO₄ prepared with Li:Fe:P = 3:1:1.2 shows the lowest phosphate content (Li:Fe:P = 1.026:1:0.781), while Li content also changes less. According to these results, to approach the stoichiometric ratio, as well as high purity of crystal phase and preferable morphology, the reactants with Li:Fe:P ratio of 3:1:1 is suggested.

Concentration generally plays significant role on particle size and morphology, while interestingly the dependency of species on concentration is observed in our study.

As shown in Fig. 4a, the precipitations prepared with Li:Fe:P = 3:1:1.2 and Li:Fe:P = 3:1:1 both show obvious impurities when [Fe²⁺] is 0.1 M. The impurities appear when the dosage of

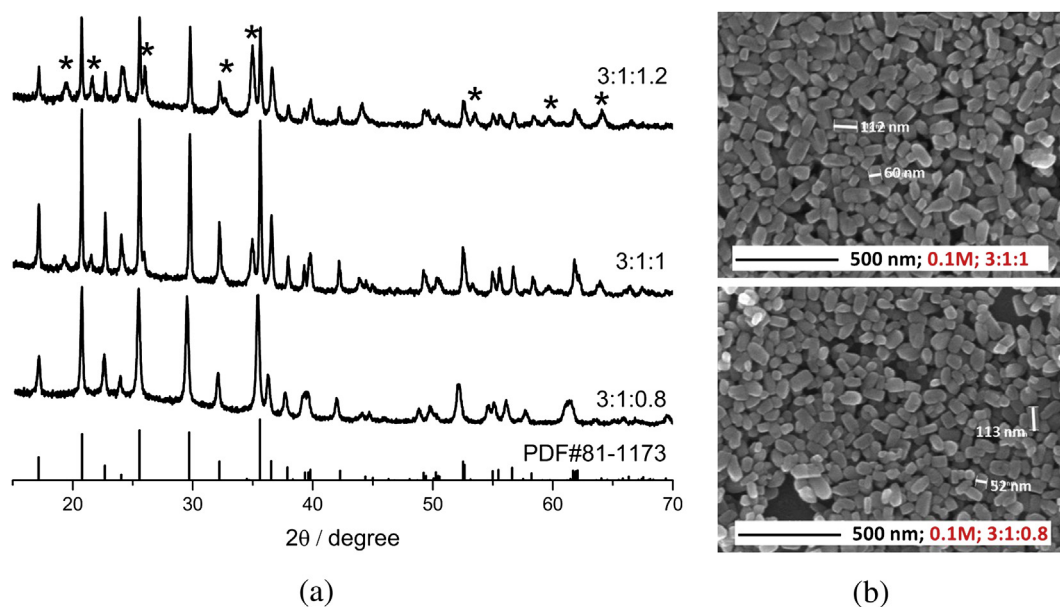


Fig. 4. XRD patterns and corresponding SEM micrographs of solvothermal LiFePO₄ with different mole ratio of reactants, with [Fe²⁺] = 0.1 M at 180 °C for 10 h (a) XRD patterns; (b) SEM micrographs.

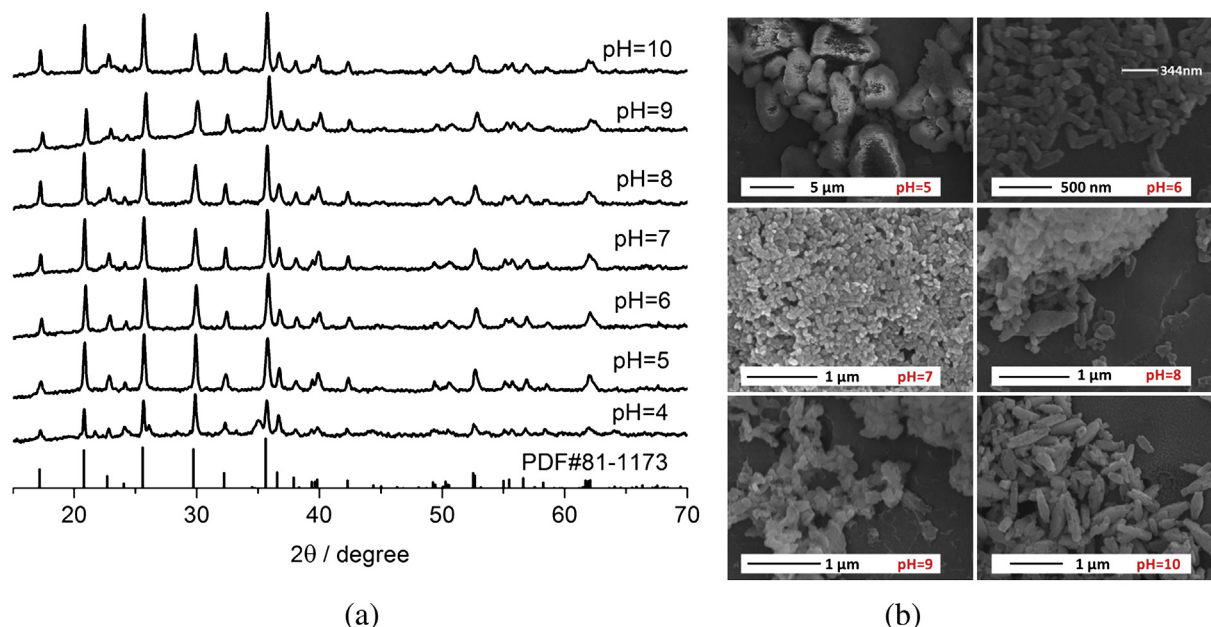


Fig. 5. The LiFePO₄ particles after glycol solvothermal reaction of 12 h at 180 °C. The starting solutions are adjusted to be different pH values. (a) XRD patterns; (b) SEM images.

phosphoric acid increasing. However, these impurities cannot be distinguished by SEM. As shown in Fig. 4b, the LiFePO₄ particles prepared with Li:Fe:P = 3:1:1 and Li:Fe:P = 3:1:0.8 are all neat and well mono-dispersed. What is more, their morphology and particle size are very similar. This reminds us that though the electrochemical performance are the most convinced criterion for LiFePO₄ evaluation, a reasonable understanding among reaction condition and products is more essential for process control.

Fig. 5 shows the XRD patterns and corresponding SEM images for the LiFePO₄ particles prepared in solutions with different pH value. Except the sample prepared when the pH is 4, all the XRD reflections in all the other samples can be indexed on the basis of an orthorhombic olivine-type LiFePO₄ structure without any detectable impurity phases (Fig. 5a). The changes in crystalline orientation can be observed according to the relative peak density, and it can be confirmed further from Fig. 5b. The LiFePO₄ particles present totally different shape, size and aggregation, indicating a dramatic influence of pH value. A neutral solution is more preferred based on these results.

High temperature and long duration are benefit for crystallization. As shown in Fig. 6, the unit cell volume of as-prepared LiFePO₄ particle approaches to the standard (PDF-83-2092) gradually with temperature increasing, though the differences among the unit cell volumes for different temperatures are not very significant. In particular, for the samples prepared at temperatures higher than

180 °C, their unit cell volumes are quite close and the differences are comparable with refinement error, this observation is similar to synchrotron X-ray diffraction investigation on in situ hydrothermal synthesis of LiFePO₄ [29]. In the cases of duration, the unit cell volume increases obviously with time accumulating, and slows down when the duration is longer than 480 min, indicating that poor crystalline will be obtained when the time is less than 480 min. Comparing with temperature and duration, pH shows more week influence on crystallinity. It seems from Fig. 6c that neutral solution is desired to get LiFePO₄ particles with high crystallinity.

Fig. 7a compares the charge–discharge profiles for the 1st, 30th, 60th and 100th cycle. After carbon coating, LiFePO₄ particles, which prepared with Li:Fe:P = 3:1:1 at 180 °C for 10 h, exhibit a high initial discharge and discharge capacity of 161 mAh g^{−1} and 162 respectively, which are close to the theoretical value of 170 mAh g^{−1}. The initial columbic efficiency is 99.4% and the difference between the charge and discharge curves is very little as seen in Fig. 7a, indicating the high purity of the olivine LiFePO₄ structure and adequate electronic conductivity. In the following cycles, it present little difference of the charge/discharge curves during cycling, indicating that irreversible structure evolution or side reactions does not happen during cycling. Accordingly, this LiFePO₄ sample exhibits excellent cycleability with no noticeable fade and very high columbic efficiency in 100 cycles, as seen in Fig. 7b. Coloumbic efficiency is near 100%, which plays very important role for the

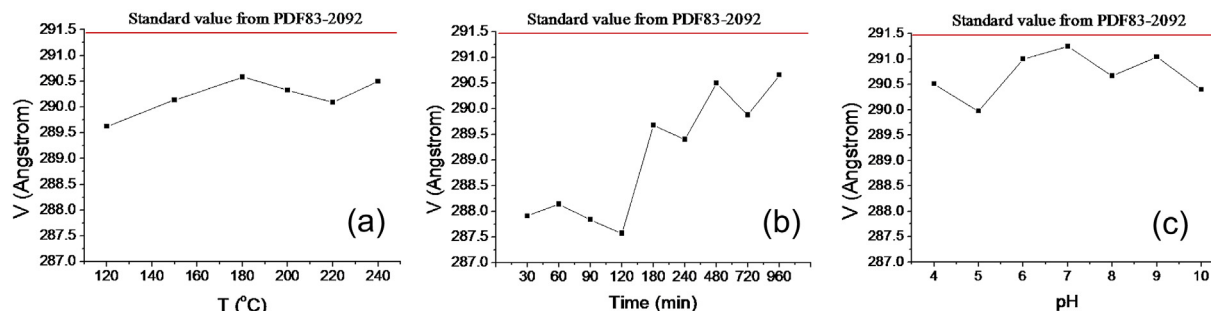


Fig. 6. The unit cell volume as a function of preparation condition. The unit cell volume is determined from Rietveld refinement.

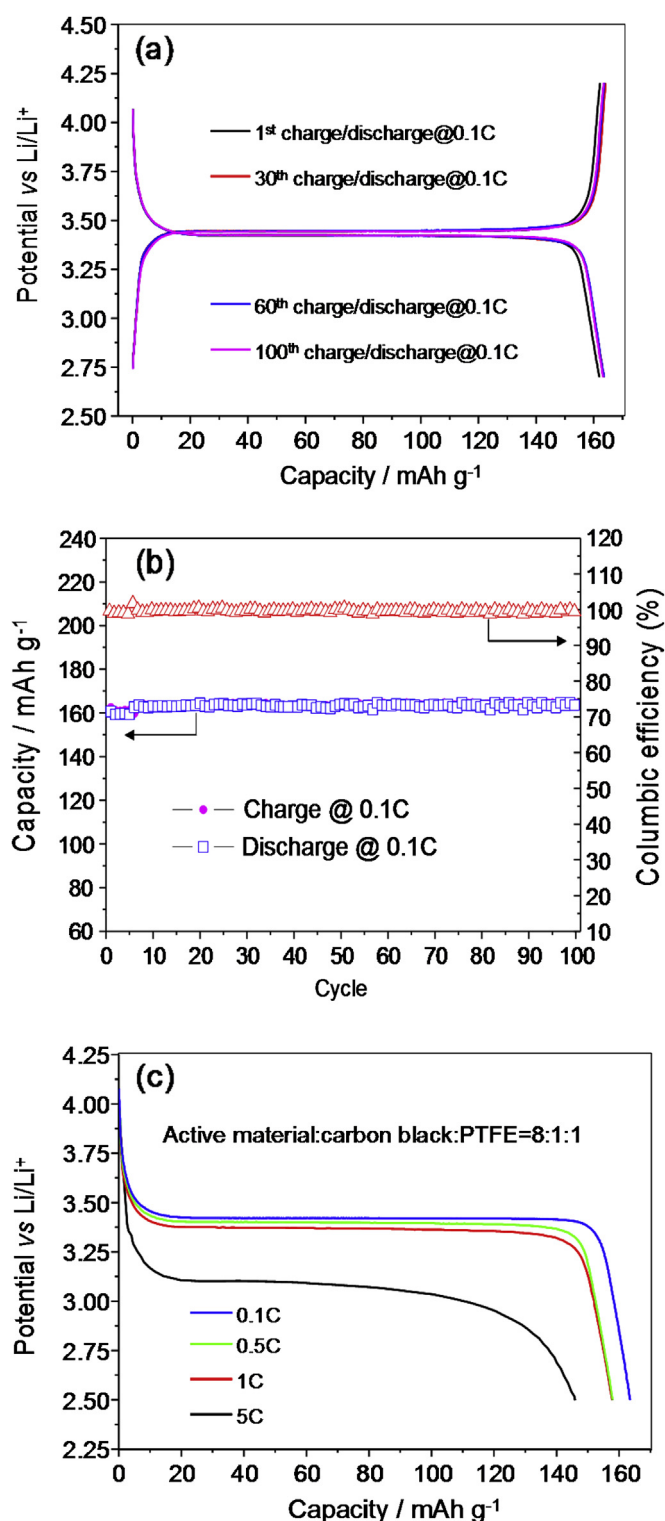


Fig. 7. (a) Changes in charge/discharge profiles as function of cycle; (b) cycling performance at 0.1 C rate; (c) C-rate performance. The electrode formula is 80% LiFePO₄/C composites, 10% carbon black and 10% binder. Discharge rate capability after charging at C/10 at upper cut-off voltage of 4.2 V. C/n denotes the rate at which a full discharge takes n hours. The loading density of the electrode is 17 mg cm⁻². The voltage window is 2.0–4.2 V.

cycling life of a practical battery [30]. The rate capability of this LiFePO₄ sample is evaluated with loading density of 17 mg cm⁻², as shown in Fig. 7c. The reversible capacities delivered are 164 mAh g⁻¹, 158 mAh g⁻¹ and 147 mAh g⁻¹ at 0.1 C, 1 C and 5 C, and

the discharge plateau is above 3 V versus Li⁺/Li, indicating good performance as reported elsewhere [31,32]. The excellent capacity, cycleability and rate capability of the LiFePO₄ sample prepared by solvothermal may be favored from both the nano-sized (80 nm long and 30 nm wide) and the good crystallinity [23,33,34]. In this sense, ethylene glycol based solvothermal process may pave a promising way to prepare high performance nano LiFePO₄.

4. Conclusions

LiFePO₄ particles with average size of 80 nm long and 30 nm wide, highly pure olivine structure and high dispersity can be prepared by solvothermal with ethylene glycol as solvent without any reductant. What is more, the solvothermal conditions, including temperature and duration, show little effect on the crystal structure, particle size and morphology, indicating a good robustness for industry production. The proposed ethylene glycol based solvothermal process may pave a promising way to prepare high performance nano LiFePO₄. On the other hand, the ratio and concentration of reactant and the pH value of the process show significant effect on the purity, crystal structure, particle size and morphology, which in turn endow a wide possibility for product tuning. In particular, LiFePO₄ particles prepared by this solvothermal process exhibit a reversible capacity of 164 mAh g⁻¹, as well as high cycleability and good rate capability. So ethylene glycol based solvothermal process is a promising strategy for industry production of LiFePO₄ with high performance.

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